



Short communication

Li metal utilization in lithium air rechargeable batteries



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HIGHLIGHTS

- Reducing the Li metal amount will offer anode effects on the performance.
- Realization of theoretical specific energy density was confirmed on Li-air batteries.
- Low cycle stability was attribute to Li dendrite formation during cycle.

ARTICLE INFO

Article history:

Received 23 October 2012

Received in revised form

7 January 2013

Accepted 9 January 2013

Available online 21 January 2013

Keywords:

Li-air battery

Li usage

Cycle stability

Li dendrite formation

ABSTRACT

Effects of Li amount used for anode on the discharge capacitance of a lithium-air battery were studied in order to investigate the effects of Li usage. On the basis of Ketjenblack air electrode, electrochemical analysis were performed in the voltage range of 4.5–2.0 V. Because the amount of Li limits the overall discharge capacity, the capacity decreases with decreasing the Li amount in the cell. Although only 370 mAh g⁻¹ (gram of air electrode) of capacity was obtained by reducing the Li amount to 0.9 mg, almost 100% of Li can be used for discharge and it is corresponded to 4111 mAh g⁻¹ (gram of Li) with reasonable cycle stability. To confirm the residual amount of Li on anode, ICP measurement was performed after first discharge. Decrease in capacity with cycle number can be assigned to the decreased amount of Li dissolved and this could be related with formation of dendrite and porous Li deposition.

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1. Introduction

Recently, there has been sharply increased attention to lithium-air rechargeable batteries because of its high theoretical specific energy density, which is a desirable characteristic for high energy density requested for electric, hybrid, and plug-in hybrid vehicle. The theoretical specific energy density (excluding oxygen) is 11,140 Wh kg⁻¹, which is much higher than that of other advanced batteries [1]. The use of metallic lithium could make it possible to have high theoretical specific energy density value with very simple mechanism. During the discharge reactions, lithium ions dissolve into the electrolyte ($\text{Li} \rightarrow \text{Li}^+ + e^-$) from the Li metal anode, and oxygen reduction was occurred on air electrode. When oxygen reduction reaction is occurred, the processes are so complex depending on the type of electrolyte. Several recent papers have focused on the discharge chemistry and revealed that Li_2O_2 is

a principal product when stable electrolyte is used [2,3], however, in some case, Li_2O_2 is converted to Li_2CO_3 [4,5] resulting in low cycle stability. Further studies have been concentrated on the effects of catalyst to reduce the over-potential [3,6], high capacity, and lowering the charge potential [7,8]. Although large parts of studies on lithium-air battery are performed on air electrode or liquid electrolyte, usage of Li metal is another critical important issue in lithium-air batteries for realizing high energy density. However, in previous studies, researches about Li metal electrode are still not thoroughly studied, especially utilization of Li metal for discharge. Although importance of Li metal on the lithium-air battery system [2,9] is reported, number of research on the details of anode electrode was limited up to now. On the other hands, it is well known that dendrite forms on anode during charge for metal-air battery and this causes problems for cycle stability of metal-air rechargeable battery. Therefore, studies on change in morphology of anode are highly important for metal-air rechargeable battery. Therefore, in this study, we investigated the Li metal utilization to confirm whether all Li can be used for discharge when capacity of air electrode is large enough. This is simply done by increasing ratio of

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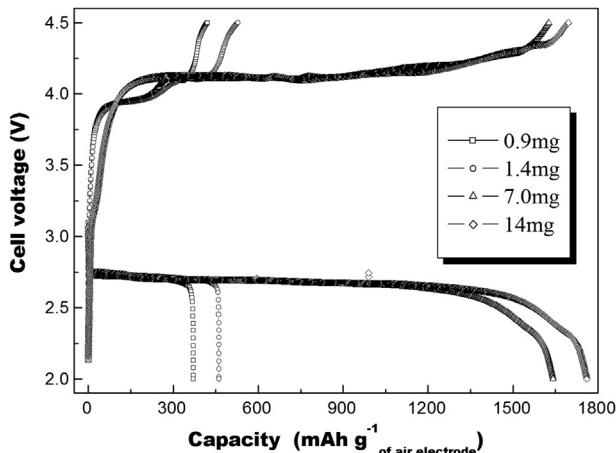


Fig. 1. Charge–discharge curves of lithium–air batteries using Ketjenblack based air electrode with various amounts of Li as an anode.

cathode to anode weight. Effects of surface morphology change of Li metal on cycle stability are also studied.

2. Experimental

Charge and discharge property of lithium–air batteries were measured by using Swagelok-type cells. The cathodes for the lithium–air batteries were prepared by casting a mixture of Ketjenblack (EC600JD, LION Co. Ltd), manganese oxide powder (EMD, Denka Co. Ltd.), and PTFE as a binder with a total ratio of 85:5:10. The electrode mixture was pressed onto a stainless steel mesh and the cathode was dried at 160 °C under vacuum oven for 5 h. Various amounts of Li foil (thickness: 0.1 mm, Shinjo Metallic Co. Ltd.) were used as the anode and separated by two pieces of glass fiber separator (Toyo Roshi Kaisha Ltd, ADVANTEC). The mixed solution of ethylene carbonate and diethyl carbonate (3:7 by volume) including lithium salts of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as an electrolyte. All cells were gas-tight excepting for the stainless steel mesh windows to adopt 1 atm of oxygen gas. To verify Li remaining after the first discharging, ICP analysis was performed by PerkinElmer, Optima 5300DV for determining the change in Li usage. After first discharge, the cell was disassembled in a glove-box filled with Ar gas, and then anode

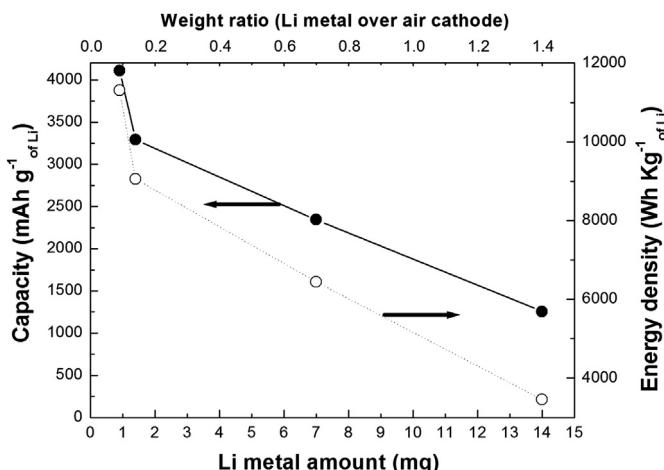


Fig. 2. Specific capacity and energy density as a function of Li amount in the lithium–air batteries using Ketjenblack air electrode.

Table 1
ICP analysis of anode using 0.9 mg of lithium after first discharge.

	Initial Li metal amount	Li metal remains
Volumetric amount	180 mg L⁻¹	0.279 mg L⁻¹
Practice amount on anode	0.9 mg	1.48×10^{-3} mg

mesh was washed in a PC solution to remove the Li effect from electrolyte. The dried mesh in the glove-box was dipped into water and then Li amount in water was measured with ICP.

3. Results and discussion

In order to investigate the Li amount effects on the discharge capacity of lithium–air batteries, various amounts of Li metal were used as the anode and Ketjenblack was used as the cathode electrode mixed with EMD and PTFE. It is also noted that the weight of cathode was always fixed 10 mg in this study. Electrochemical reaction between oxygen and lithium occurs on the surface of the carbon. Therefore, Ketjenblack was usually chosen for the air electrode material [7]. Fig. 1 shows the charge and discharge curve at initial cycle with different amount of Li for anode. In this figure, discharge and charge capacity were expressed by air electrode base. Unless otherwise noted, 14 mg of Li, which was pressed onto a stainless steel mesh, was used for a counter electrode of the lithium air battery. This cell was denoted as an ordinary cell in the following part. In case of discharge curves of samples, all cells show potential plateau at 2.75 V stably. The discharge capacity of 1760 mAh g⁻¹ (gram of air electrode), which is corresponded to ca. 33% of Li utilization, could be obtained in case of an ordinary cell. In order to obtain the specific

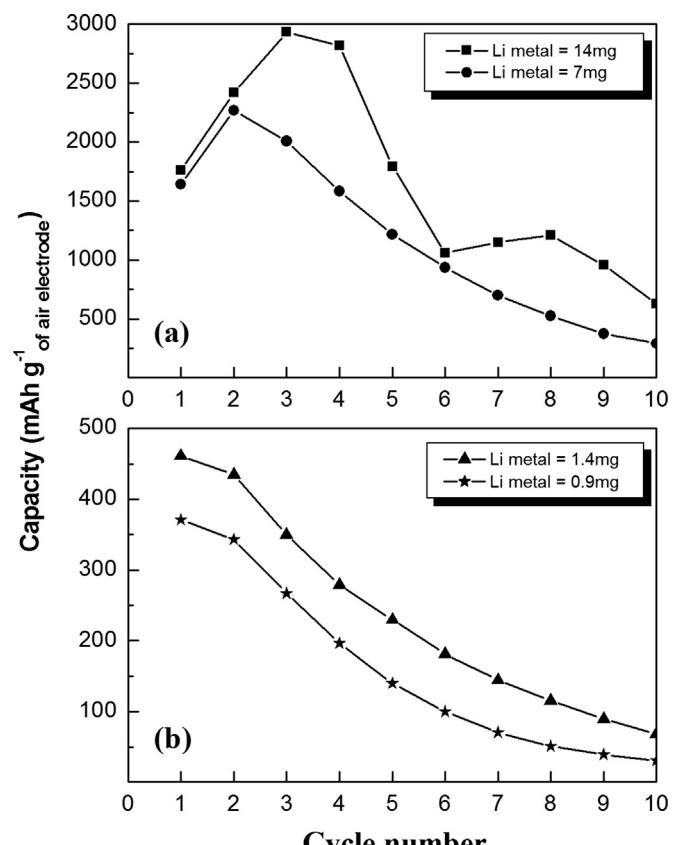


Fig. 3. Cycle retention rate of lithium–air batteries using Ketjenblack based air electrode with various amounts of Li. The amount of air electrode used is 10 mg.

capacity of lithium-air batteries, discharge capacity is normalized by the weight of cathode electrode which including Ketjenblack, EMD and PTFE in this study. By reducing the Li amount, discharge capacity decreased to 1640, 461, and 370 mAh g⁻¹ with 7, 1.4, and 0.9 mg of Li metal used respectively. Because of sufficient supply of Li amount, most of the studies of a lithium-air battery are suffered capacity decrease from cathode limitation [6–8,10–12]. Although the ordinary cell shows about 33% Li utilization rate, efficiency could be increased to about 100% by decreasing the Li amount. In case of the cell using 0.9 mg of Li, it showed a high Li usage about 100%, which means all amount of Li could be used for discharge. Therefore, if the capacity of air electrode is large, then almost all Li could be realized for discharge capacity.

Fig. 2 shows the specific capacity as a function of Li amount over cathode weight. It can be seen that capacity of 1257 mAh g⁻¹ (gram of Li) was achieved when we used 14 mg of Li for the anode. As discussed, with decreasing Li amount to 0.9 mg, 4111 mAh g⁻¹ (gram of Li) capacity, which is slightly higher than the theoretical capacity could be obtained. Li salt in electrolyte may also contribute the discharge process resulting in the larger capacity. Therefore, the reason for the slightly higher capacity than theoretical value about 3860 mAh g⁻¹ might be explained by contribution of Li in electrolyte for discharge.

In order to confirm the remained amount of Li after the first discharge, especially in the cell using 0.9 mg of Li, ICP measurement was performed by using the anode taken from the cell after discharge. As shown in **Table 1**, the initial amount of Li in the cell is 180 mg L⁻¹. However, the amount of Li on anode after first discharge was 0.279 mg L⁻¹ which corresponded to only 0.15% of initial Li amount. These results suggest that all Li could be used for discharge when Li amount is 0.9 mg which is corresponded to 0.21 times smaller molar ratio to Li amount deposited on air electrode calculated from 1760 mAh g⁻¹ (gram of air electrode) which is observed capacity in

case of sufficient of Li in the cell. Therefore, it is clear that air electrode has a sufficient capacity for Li oxidation in case of 0.9 mg Li.

Capacity retention rate of lithium-air batteries with various Li metal amounts is also studied and **Fig. 3** shows the capacity as a function of cycle number. Because of large difference in capacity, we show the cycle stability of the cell with two figures. In case of the cell with enough amount of Li which is shown in **Fig. 3(a)**, the capacity decreased excepting for initial few cycles. This decrease in discharge capacity was also reported by several groups and it is considered that poor cycle stability was attributed to Li₂CO₃ formation and electrolyte decomposition [4,8]. Similarly with **Fig. 3(a)**, the cell with small amount of Li in **Fig. 3(b)** also shows low cycle stability, however, decrease in capacity is much faster comparing with the cell with sufficient amount of Li. Faster decrease in discharge capacity could be explained by the several reasons, i.e., decrease in air electrode activity faster, decomposition of electrolyte easier, and formation of dendrite in Li anode results in decreased amount of Li for discharge. Considering that coulomb efficiency is almost 100% for each cycles and small discharge capacity at decreased Li amount, it is reasonably considered that amount of Li contributes to discharge decreases with increasing cycle number. Since Li dendrite formation becomes more significant with increasing usage of Li, decreased amount of Li for discharge seems to be reasonable. In fact, Li on anode side was observed in all cells after discharge of cycle stability measurement.

Fig. 4 shows SEM images of Li metal surface with various Li contents after 10 time cycles of discharge and charge reactions. The formation of dendrite with needle like shape was observed in all samples (pointed out by white arrows). However, in spite of the concerns, formation of dendrite is not serious on all samples. Comparing with the cell with low Li utilization, formation of dendrite is more serious with high Li usage and the morphology of the deposited Li is more porous. Therefore, low cycle stability of the cell

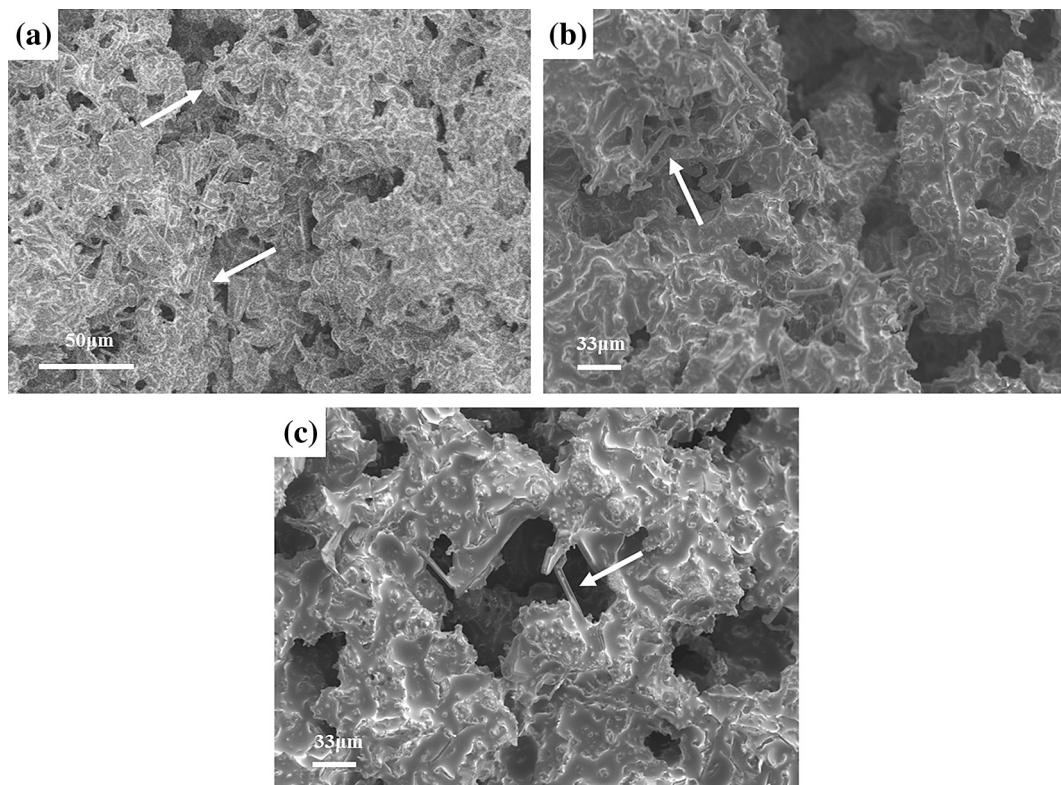


Fig. 4. SEM images of Li metal electrode surface after 10 cycles; (a):Li = 0.9 mg, (b): Li = 7 mg and (c):Li = 14 mg. The amount of air electrode used is 10 mg.

at high Li usage could be assigned to the change in morphology of Li anode. For improving the cycle stability at high Li utilization, preventing Li dendrite formation and porous structure is strongly requested.

4. Conclusions

The purpose of this study is to investigate the effects of Li amounts on electrochemical performance of Li-air battery and it was confirmed that realization of theoretical specific energy density is achieved on a lithium-air battery system in a case of large capacity of air electrode for Li oxide deposition. By variation of Li amount from 14 to 0.9 mg, the discharge capacity decreased with decreasing Li amount on the anode from 1760 to 370 mAh g⁻¹, respectively. However, the efficiency of Li usage to the capacity was significantly increased to ca.100% when 0.9 mg of Li metal was used (Cathode:Anode = 10:0.9 weight ratio). On the other hand, cycle stability of the cells decreased with increasing Li utilization and this could be explained by the formation of dendrite and porous Li. Therefore, by control of Li deposition morphology in

charge process, both high energy density and cycle stability may be achieved.

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